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Diffusion barrier properties of tungsten nitride films grown by atomic layer deposition from bis(*tert*-butylimido)bis(dimethylamido)tungsten and ammonia

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Highly uniform, smooth, and conformal coatings of tungsten nitride (WN) were synthesized by atomic layer deposition (ALD) from vapors of bis(*tert*-butylimido)bis(dimethylamido)tungsten and ammonia. The films are shiny, silver colored, and electrically conducting. The films were amorphous as deposited. 100% step coverage was obtained inside holes with aspect ratios greater than 40:1. WN films as thin as 1.5 nm proved to be good barriers to diffusion of copper for temperatures up to 600 °C. Annealing for 30 min at temperatures above 725 °C converted the WN to pure, polycrystalline tungsten metal. ALD of copper onto the surface of the WN produced strongly adherent copper films that could be used as "seed" layers for chemical vapor deposition or electrodeposition of thicker copper coatings.
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Tungsten nitride (WN) is considered to be a good barrier against diffusion of copper in microelectronic circuits.[1] WN can also be used in electrodes for thin-film capacitors and field-effect transistors.[2] WN has been made by reactive sputtering, but the uniformity of film thickness inside narrow features ("step coverage") is not expected to be adequate for use in future microelectronic devices having narrow features with high aspect ratios.[3]

Atomic layer deposition (ALD) (also known as atomic layer epitaxy) is a process for depositing thin layers of solid materials from two or more vapor precursors.[4] The surface of a substrate onto which film is to be deposited is exposed to a dose of vapor from one precursor. Then any excess unreacted vapor from that precursor is pumped away. Next, a vapor dose of the second precursor is brought to the surface and allowed to react. This cycle of steps can be repeated to build up thicker films. One particularly important aspect of this process is that the ALD reactions are self-limiting, in that only a certain maximum thickness can form in each cycle, after which no further deposition occurs during that cycle, even if excess reactant is available. Because of this self-limiting character, ALD reactions produce coatings with highly uniform thicknesses. Uniformity of ALD film thicknesses extends not only over flat substrate surfaces, but also into narrow holes and trenches. This ability of ALD to make conformal films is called "good step coverage."

Coatings of WN made by ALD from WF_6 and NH_3 have good step coverage.[5] A disadvantage of this process is that WF_6 and/or its reaction byproduct, HF, attacks substrates made of Si or SiO_2. Also, this process can leave the WN_x surface with a fluorine residue that may impede adhesion of copper to the surface. In particular, adhesion of Cu deposited by chemical vapor deposition (CVD) is often considered to be poor in part because of fluorine contamination at the interface between the tungsten nitride and the copper.

In the present work, WN barrier films were made by ALD using bis(*tert*-butylimido)bis(dimethylamido)tungsten, $({}^{t}\mathrm{BuN})_2(\mathrm{Me}_2\mathrm{N})_2\mathrm{W}$, and ammonia at low substrate temperatures (250–350 °C). The basic bulk properties of these films were investigated, as well as their performance as a barrier to the diffusion of copper.

The flow reactor shown in Fig. 1 was used to deposit the tungsten nitride coatings by ALD. Bis(*tert*-butylimido)bis(dimethylamido)tungsten(VI),[6] with a vapor pressure of 0.037 Torr at 30 °C, was placed in a stainless steel container (W). A detailed description of the ALD system is given elsewhere.[6]

The thickness per cycle values for ALD WN films, as determined by scanning electron microscopy (SEM), was 0.05 nm at 300 °C, and 0.1 nm at 350 °C.[7] Both growth rates are smaller than an ideal monolayer (ML)/cycle. (With the atomic density of tungsten nitride $d = 5.68 \times 10^{22}\ \mathrm{cm}^{-3}$, 1 ML can be defined as $d^{-1/3} = 0.26$ nm by assuming simple

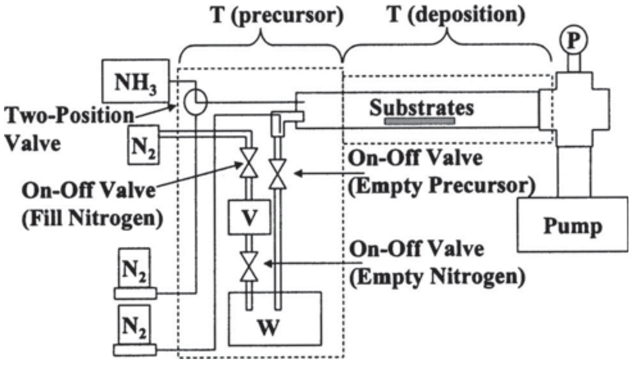

FIG. 1. Schematic diagram of the deposition system showing the location of the nitrogen mass flow controllers and the nitrogen source (N_2), the ammonia vapor reservoir (NH_3), the two-position, three-way gas-chromatography valve, the three on-off diaphragm valves, the nitrogen assist dose volume (V), the tungsten precursor (W), the pressure measurement (P), and the rotary vane pump (pump) with respect to the precursor [T(precursors)] and deposition [T(deposition)] isothermal heating zones.

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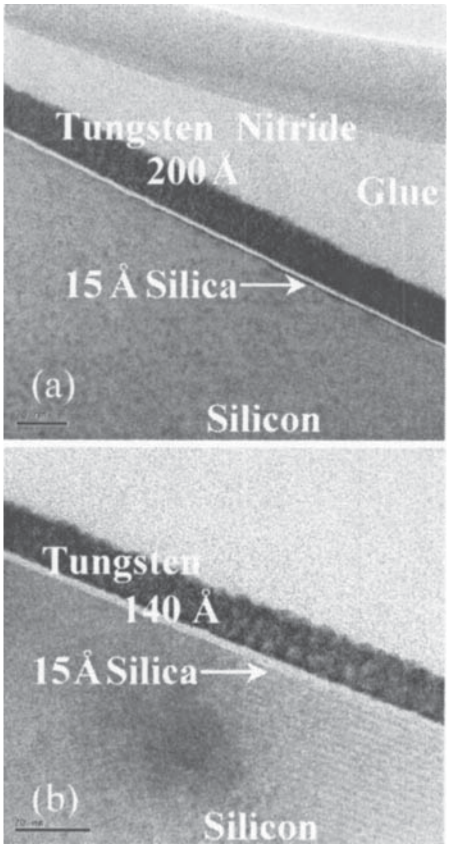

FIG. 2. (a) HRTEM image of a 20-nm-thick tungsten nitride film as deposited at 300 °C (400 cycles). The reference bar is 20 nm long. (b) HRTEM image of a 14-nm-thick tungsten film. Note that the film has fully crystallized and that it has shrunk from 20 nm [see Fig. 2(a)] to 14 nm (about 30%). The reference bar is 20 nm long.

cubic packing.) This is probably due to the steric bulk of the $(^t\mathrm{BuN})_2\mathrm{W}(\mathrm{NMe})_2$ limiting the surface adsorption density.

The films are pure tungsten nitride. Rutherford backscattering spectroscopy[8] (RBS) showed that there was no appreciable oxygen in the film. Carbon was less than the detectable limit, $<\frac{1}{2}$ at. %. X-ray photoelectron spectroscopy[9] (XPS) confirmed that no carbon was detectable in the film (detection limit $<\frac{1}{4}$ at. %). The films were silver and shiny. The density of the material was found to be about $12\ \mathrm{g/cm^3}$ by combining RBS and SEM data. RBS determined the chemical composition of the film to be $\mathrm{WN}_{1.1\pm0.1}$. X-ray diffraction[10] (XRD) confirmed that once the as-deposited amorphous films were annealed they contained the diffraction peaks corresponding to the known cubic, crystalline phase of WN.[11,12] The x-ray diffraction peaks were still very broad for the crystallized material, indicating that the film is composed of nanograins smaller than 20 Å.

The WN films possessed very smooth surface characteristics. Atomic force microscopy[13] (AFM) confirmed that the surface roughness of the deposited layer (rms roughness $=0.33$ nm) was very similar, if not equal to that of the substrate (rms roughness$=0.2$–0.3 nm) on which it was deposited. The RMS roughness was independent of film thickness. SEM also showed that the films were smooth and featureless. XRD showed that the as-deposited layer was amorphous. This structural information was confirmed by high-resolution transmission electron microscopy (HRTEM),[6,14] which showed the film to be amorphous [Fig. 2(a)].

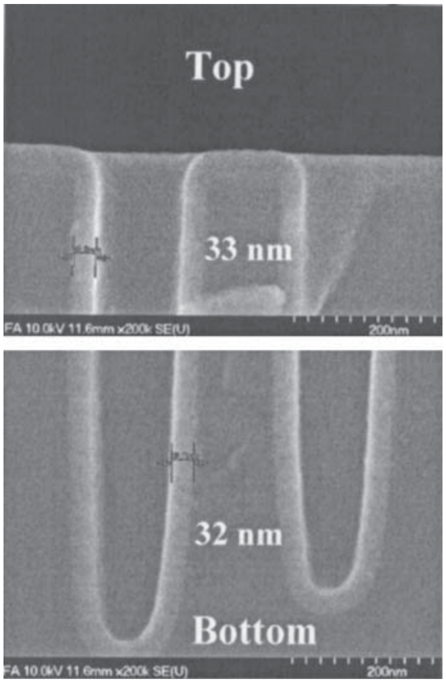

FIG. 3. A cross-sectional scanning electron micrograph of holes 0.18 μm in diameter and 7.3 μm deep in a silicon wafer uniformly coated with a 33-nm-thick tungsten nitride film as deposited at 300 °C (600 cycles). An exposure of approximately 2.1×10^4 langmuirs/cycle was used for the tungsten precursor and 2.9×10^7 langmuirs/cycle for ammonia.

A SEM picture was taken of a wafer with narrow holes (0.18 μm in diameter and 7.3 μm deep) having aspect ratio greater than 40:1 coated with WN and then cleaved to show a cross section of the coated holes. The SEM in Fig. 3 shows that the walls of the narrow hole are covered with a perfectly conformal coating. This result demonstrates the excellent step coverage achieved by ALD utilizing this new tungsten precursor.

The resistivity[15] of typical ALD tungsten nitride coating is about 1.5×10^{-3}–$4.0\times10^{-3}\ \Omega$ cm. The resistivity was reduced to 4.8×10^{-4}–$9.6\times10^{-4}\ \Omega$ cm by annealing in forming gas at 700 °C for 30 min to form the polycrystalline WN phase. The resistivities were even further reduced to 1.2×10^{-4}–$5.0\times10^{-4}\ \Omega$ cm when the films were annealed at temperatures greater than 725 °C for 30 min. The annealed film, at temperatures greater than 725 °C, lost its nitrogen to become pure tungsten metal and crystallized to the cubic tungsten structure. RBS and XPS confirmed the loss of nitrogen. XRD too confirmed that once the as-deposited amorphous films were annealed at temperatures greater than 725 °C, they contained the diffraction peaks corresponding to the known cubic, crystalline phase of W.[12,16] A decrease in thickness (30%) occurred as the films turned from WN into the more dense W films. This decrease in thickness can be seen by comparing the HRTEM images of the same sample before annealing, when the film is still just WN [Fig. 2(a)], and after annealing, when the film has turned to pure W metal [Fig. 2(b)]. The polycrystalline W films remained smooth as was seen by AFM (rms roughness$=0.34$ nm). The annealed films remained adherent to the substrates.

When the tungsten nitride film was deposited directly on silicon, without an oxide interlayer produced by the UV-ozone treatment, annealing the WN to a temperature of

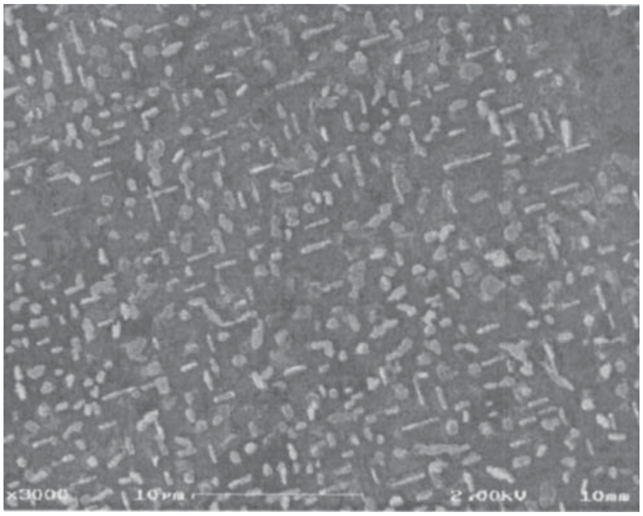

FIG. 4. A sample annealed at 650 °C showed numerous crystals of copper silicide due to the complete breakdown of the barrier.

1000 °C produced an interfacial layer of tungsten silicide, identified by RBS.[12]

The ALD tungsten nitride films were shown to be good barriers to the diffusion of copper by the following tests. 100 nm of copper was sputtered on top of various films of tungsten nitride ranging in thickness from 1.5 to 100 nm on silicon substrates. Samples of these Si/WN/Cu structures were annealed in forming gas for 30 min at various temperatures. The copper on the surface was dissolved in nitric acid solution, and then the tungsten nitride was dissolved in ammonia/hydrogen peroxide solution. Examination of the silicon by SEM and RBS showed no change in samples annealed at 450, 500, 550, or 600 °C. A sample annealed at 600 °C showed a few bright crystals of copper silicide due to isolated breakdown of the tungsten nitride barrier at a few defect sites. (None of these experiments were done in a cleanroom.) A sample annealed at 650 °C showed numerous crystals of copper silicide due to complete breakdown of the barrier (Fig. 4). These results are conventionally interpreted to mean that the tungsten nitride is stable to 600 °C and is an excellent barrier to the diffusion of copper.

Copper oxide was deposited on tungsten nitride films by ALD from 1000 cycles of alternating exposure to copper(II) bis(*sec*-butylacetoacetate) vapor and an ozone/oxygen gas mixture at a substrate temperature of 300 °C using an apparatus described by Fig. 1 with the copper precursor in the "ALD bubbler" and the ozone/oxygen mixture from an ozone generator passing through the two-position valve. Copper oxide (CuO) was deposited at a rate of about 0.05 nm per cycle. The copper oxide was reduced to copper metal by heating the sample to 500 °C in a hydrogen atmosphere for 30 min. The resulting shiny copper layer adhered strongly to the tungsten nitride, and could not be removed by adhesive tape applied to the copper. This thin ALD copper could be used as a "seed" layer to initiate CVD or electrodeposition of copper.

In conclusion, tungsten nitride films were synthesized from vapors of tungsten bis(*tert*-butylimide) bis(dimethylamide) and ammonia gas supplied in alternate doses to surfaces heated to 250–350 °C. This process produced coatings of tungsten nitride having very uniform thickness and excellent step coverage in holes with aspect ratios up to at least 40:1. The films are metallic electrical conductors. Suitable applications in microelectronics include barriers to the diffusion of copper and electrodes for capacitors. Films as thin as 1.5 nm proved to be good barriers up to 600 °C.

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[7] Thickness measurements and step coverage (on cleaved samples) were made by SEM (Leo 982; resolution of ±3 nm).
[8] Composition and number of atoms per unit area were determined by RBS (General Ionics model 4117, 1.7 MeV Tandetron) of samples grown on glassy carbon substrates.
[9] Composition was also verified by XPS (Surface Science Lab SSX-100) and energy dispersive x-ray spectroscopy (JEOL 2010F equipped with an energy dispersive x-ray spectrometer).
[10] XRD (Scintag model XDS2000) and electron diffraction by transmission electron microscopy (JEOL 2010F) determined that the films are amorphous.
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[13] Roughness measurements were made by AFM (Nanoscope III and IV, Digital Instruments). Surface morphology was also determined by SEM.
[14] High-resolution transmission electron microscopy were measured on a JEOL 2010F.
[15] Electrical resistivities were obtained on glass substrates using a four-point probe (Veeco model No. FPP-100).
[16] Swanson, Tatge, Natl. Bur. Stand. (US). Circ. 539, I, 28 (1953).